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A REVIEW ON EXTRACTION PROCESSES OF LIGNOCELLULOSIC CHEMICALS FROM OIL PALM BIOMASS

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ABSTRACT

Oil palm biomass (OPB) is a by-product derived from the oil palm industry; periodically available in the field during the replanting and pruning activities; and from the milling processes of palm oil. The biomass includes oil palm trunk (OPT), oil palm frond (OPF), kernel shell, oil palm empty fruit bunch (OPEFB), oil palm mesocarp fibre (OPMF), and palm oil mill effluent (POME). OPB is classified as lignocellulosic residues that typically contain cellulose, hemicellulose, and lignin in their cell wall that can be converted into fine chemicals. These lignocellulosic chemicals have significant potential applications in food, chemicals and pharmaceuticals industries. A number of different types of extraction technologies have been developed; namely chemicals, physico-chemicals, biochemicals or the combinations of these processes. But as the methods that are environmental-friendly are the current trend, this article has its focus entirely on green technologies. This article comprehensively reviews the conversion of OPB into lignocellulosic chemicals with special attention on various extraction processes, followed by discussion on their special merits as well as their weaknesses. Sustainability for each of the process is also considered in detail in the discussion.

Keywords: oil palm biomass, lignocellulosic chemicals, cellulose, extraction process.

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INTRODUCTION

Malaysia has established its name as a large producer and exporter of palm oil in the world, second only to Indonesia. The oil palm industry in Malaysia, spanning 5.74 million hectares of plantation and 453 palm oil mills, produced over 17.32 million tonnes of oil and almost 100 million tonnes of biomass (MPOB, 2016). Oil palm biomass (OPB) is a by-product derived from the oil palm industry; periodically available in the field during the replanting and pruning activities; and from the milling processes in the palm oil mills. The biomass includes oil palm trunk (OPT), oil palm frond (OPF), kernel shell, oil palm empty fruit bunch (OPEFB), oil palm mesocarp fibre (OPMF) as well as palm oil mill effluent (POME) comprising of sludge water as well as some solids made up of debris from palm fruit mesocarp. Based on the formula used in the estimation of oil palm biomass extractable per hectare of plantation (Astimar *et al*., 2011), in the year 2016, from 84 769 ha of replanting about 6.32 million tonnes (dry weight) of OPT were felled for replanting and 61.20 million tonnes (dry weight) of OPF were also produced during pruning and replanting from the plantation. In 2016, 453 palm oil mills in Malaysia processed 85.84 million tonnes of fresh fruit bunches (FFB) generating approximately 6.61 million tonnes (dry weight) of OPEFB, 6.95 million tonnes (dry weight) of OPMF and 4.01 million tonnes (dry weight) of kernel shell. An abundant quantity of biomass generation in the oil palm industry provides huge resources for the

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conversion into value-added products, as the OPB is inexhaustible, renewable, biodegradable, recyclable and a derivatisable biopolymer.

The depletion of fossil fuels and natural raw materials has encouraged the search for the development of new resource materials for the production of bio-based materials (Alekhina *et al*., 2014). OPB is classified as lignocellulosic residues that mainly comprise of cellulose, hemicellulose, and lignin in their cell wall (Raveendran *et al*., 1995). This lignocellulosic material can be converted into a valuable feedstock for the production of biosugar, biocompost, biochemical and bioethanol. Due to lignocellulosic nature of OPB, countless research and development activities are undertaken by various agencies in order to improve the transformation of OPB into more valuable substrate for producing a variety of chemicals that will have huge potential in food, chemicals and pharmaceuticals industries.

The chemical constituents in OPB are varied considerably due to their diverse origins and types (Chew and Bhatia, 2008). The chemical composition of different OPB is shown in *Table 1*.

Cellulose forms a major constituent of most OPB. Only cellulose and hemicellulose can be converted to fermentable sugars. These lignocellulosic chemicals are reinforced in a lignin matrix similar to that of other natural fibres. Recovery of these components from the OPB requires some kind of pre-treatment. The pathway of different pre-treatments on OPB to extract lignocellulosic chemicals and production of fermentable sugars is as shown in *Figure 1*.

A pre-treatment method is intended to remove lignin, reduce crystallinity of the cellulose and increase the porosity of lignocellulosic materials in order to make cellulose and hemicellulose more amenable to the hydrolysis and fermentation processes that are used to convert these lignocellulosic chemicals to fermentable sugars in higher yield (Balat, 2011; Mora-Pale *et al*., 2011; Moiser *et al*., 2005). Various pre-treatment methods have been developed to extract these lignocellulosic chemicals. These include physical pre-treatments (*e.g.* size reduction, steaming, hot water, steam explosion) chemicals methods (*e.g.* acid, alkali, organic solvents), biological treatments (enzyme and microbes) and their combination. Furthermore, interest in green extraction has been revived by the increasing public concern towards the environment. The extraction of lignocellulosic chemicals using less solvent at low concentration, less toxic and non-toxic chemicals in combination with physical treatments that are less energy intensive are considered as green methods (Rabemanolontsoa and Saka, 2016; Marzialetti *et al*., 2011; Nazir *et al*., 2013; 2012; Kumar *et al*., 2009; Quesada *et al*., 1999). Among aforementioned pre-treatment options, chemical treatment and its combination have been the most reported method for the lignocellulosic conversion into chemicals (Kumar and Sharma, 2017; Sun *et al*., 2016; Kim *et al*., 2016; Brodeur *et al*., 2011).

By recovering all the lignocellulosic chemicals in the OPB, it will not only be able to solve the disposal problem, but it can create value-added products from these oil palm industry by-products (Mohd Nasir and Saleh, 2016; Mohtar *et al*., 2015; Medina *et al*., 2015; Yonga *et al*., 2016; Norzita and Lani, 2014; Zakaria *et al*., 2014a; Nazir *et al*., 2013; Amin *et al*., 2010; Robiah *et al*., 2010; Rosnah *et al*., 2006; 2009; Astimar *et al*., 2002). This review article reviews exclusively on all techniques that have been developed and used for the conversion of OPB into lignocellulosic chemicals with a focus on various extraction processes, and discussion on their advantages and disadvantages. Insights on the sustainability of each of the process are also included in the discussion.

CHEMICAL PRE-TREATMENT

Chemical pre-treatment is one of the most promising methods to extract the lignocellulosic chemicals from biomass. It has been extensively used for

TABLE 1. CHEMICAL CONTENT IN COMMON OIL PALM BIOMASS FEEDSTOCKS

Composition	Oil palm biomass chemical composition (wt %)				
	EFB	OPF	OPT	OPMF	Kernel shell
Cellulose	38-70	40-50	22-44	39-42	13-28
Hemicellulose	10-35	23-38	12-41	9-24	21-22
Holocellulose	68-86	70-83	42-73	49-64	42-47
Lignin	13-37	18-32	18-36	21-33	44-52
Xylose	29-63	26-52	15-55	40-49	63-64
Glucose	23-66	20-67	18-32	23-29	21-22
Ash	1-6	2-8	2-4	3-9	1-2

Note: EFB - empty fruit bunch. OPF - oil palm frond. OPT - oil palm trunk. OPMF – oil palm mesocarp fibre.
Source: Mohtar *et al*. (2015); Ching and Ng (2014); Rugayah *et al*. (2014); Mohd Basyaruddin *et al*. (2012); Shinoj *et al*. (2011); Bono *et al*. (2009); Chew and Bhatia (2008); Saka *et al*. (2008); Shibata *et al*. (2008); Abdul Khalil *et al*. (2006, 2008); Law *et al*. (2007); Wan Rosli *et al*. (2007); Abdul Khalil and Rozman (2004); Law and Jiang (2001); Sreekala *et al*. (2001); Kirkaldy and Susanto (1976).

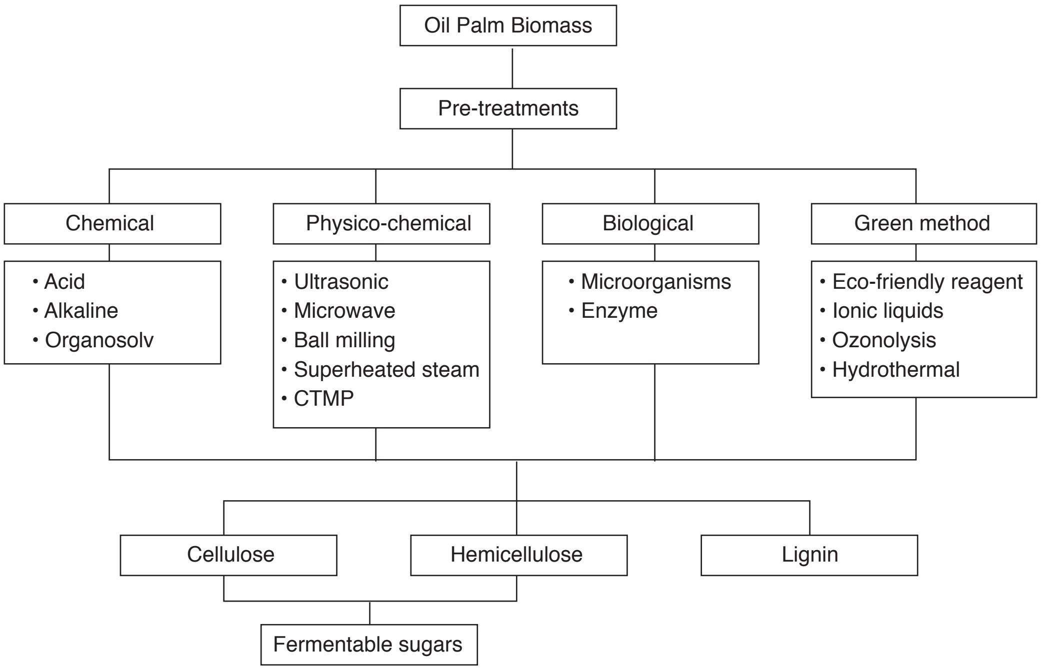

Figure 1. Pathway of different pre-treatments on oil palm biomass (OPB).

cellulosic extraction in the pulp and paper industry (Zheng *et al.*, 2009). This method also has been exploited to enhance the yield of lignocellulosic chemicals. Furthermore, there are chemicals that have been reported to have a significant effect on the structure of lignocellulosic biomass, where the pre-treatments can be carried out at room temperature and pressure but they do not produce toxic residues for the downstream processes. The chemicals used in chemical pre-treatment are selected from oxidising agents, alkali, acids and salts that are purely initiated by the chemical reactions for breaking biomass structure to degrade and/ or extract lignin, hemicelluloses and cellulose.

Acid Pre-treatment

Acids are very effective and widely known chemical that have access to glucosidic bonds in hemicellulose and cellulose in biomass. Acids have the ability to remove hemicellulose and they have been used as parts of overall processes in fractionating the components of lignocellulosic biomass (Zhang *et al.*, 2007). The pre-treatment using acid requires high temperature and pressure to achieve high yield of the targeted chemicals. The reaction also depends on several parameters like type of acid, concentration of acid and ratio of solid to liquid.

Different kinds of acid have been used such as sulphuric acid, nitric acid, hydrochloric acid and phosphoric acid. A number of studies have investigated the pre-treatment using sulphuric acid due to its high catabolic activity. Dilute sulphuric acid has traditionally been used to manufacture furfural from biomass (Esteghlalian *et al.*, 1997). This chemical pre-treatment usually involves the addition of diluted acids (range from 0.1% to 2.5% w/w) to the biomass, followed by reaction temperatures between 130°C and 210°C (Nguyen *et al.*, 2000; Saha *et al.*, 2005).

Kristiani *et al.* (2013) reported that the pre-treatment in 0.25%-2% of H_2SO_4 did increase the specific surface area of cellulose from 2.23 to 5.57 $m^2\ g^{-1}$, and also showed the decreasing crystallinity of cellulose. Other studies done by Amirkhani *et al.* (2015) showed that 94% conversion of xylose was obtained under 2% of H_2SO_4 at 120°C and 20 min of reaction times. Lignin preparation from OPEFB by successive treatment with 1% (w/w) H_2SO_4 at 121°C for 60 min and followed by treating in 2.5% NaOH at 121°C for 80 min resulting in a high lignin yield of 28.89% (Medina *et al.*, 2015).

The disadvantage of this method is the high operational and maintenance cost compared to other chemical pre-treatment (*e.g.*, dilute alkali) and physico-chemical methods [*e.g.*, steam explosion and ammonia fibre explosion (AFEX)] (Sun and Cheng, 2002; Kumar and Murthy, 2011). A suitable material for the reactor is required to withstand the corrosiveness and toxicity of the acid. An extensive washing and/or a detoxification step is also required to remove the acid before further step is taken for other product (Nguyen *et al.*, 2000; Saha *et al.*, 2005; Sassner *et al.*, 2008).

Acid pre-treatment also allows to further hydrolyse the hemicelluloses, especially xylan into sugar such as xylose, mannose, acetic acid, galactose, glucose, *etc.* In an industrial process, the reaction is always at high temperatures and pressures that lead to the degradation of glucose and xylose into furfural and hydroxymethyl furfural (HMF), respectively and also other further degradation forms such as formic acid and levulinic acid (Kootstra *et al*., 2009; Davies *et al*., 2011). Partial breakdown of lignin also leads to the formation of the phenolic compounds.

Organic acids such as maleic, oxalic, succinic, fumaric and acetic acid have been suggested as an alternative due to their relatively low acidities and high solubility to lignin. Yonga *et al*. (2016) obtained the highest yield of furfural (35.8%) after treating OPF in formic acid at high temperatures (240°C-280°C). The advantage of using organic acid is the monocarboxylic acid has lower catalytic performance due to their difference in pKa compared to dicarboxylic acids (Trzcinski and Stuckey, 2015).

Alkaline Pre-treatment

Alkali compound or salt or catalyst is widely studied in chemical pre-treatment. Various alkali reagents have been used such as sodium hydroxide (Silverstein *et al*., 2007; Wang *et al*., 2010), potassium hydroxide (Wanitwattanarumlug *et al*., 2012; Sharma *et al*., 2013), calcium hydroxide (lime) (Sierra *et al*., 2009), ammonium hydroxide (Prior and Day, 2008; Sherman *et al*., 2012), aqueous ammonia (Kim *et al*., 2009) and hydrogen peroxide or combination of these (Banerjee *et al*., 2012). Alkaline hydrolysis can be operated at lower temperature and pressure compared to other chemical pre-treatment method, but the reaction times can differ depending on the different types of biomass used (Bali *et al*., 2015). During the alkaline hydrolysis process, the structure of biomass is swelling, leading to alteration of lignin structure and breaking the ester and glycosidic chains.

Pre-treatment of OPF with aqueous NaOH (4.42%) at 100°C for 58.31 min resulted in better separation of cellulose, hemicellulose and lignin, which were 41.42%, 31.93% and 26.06%, respectively (Mohd Sukri *et al*., 2014). KOH has selectively removed xylan (Hendriks and Zeeman, 2009). Mohd Nasir and Saleh (2016) reported that they have extracted xylan from EFB in 3 M KOH at 40°C, with 4 hr of extraction time. A technology on xylooligosaccharides (XO) production from OPEFB-xylan using immobilised xylanase in a packed bed column reactor has been developed by Noorshamsiana *et al*. (2015). The OPEFB was pre-treated with KOH and the resulting xylan was further hydrolysed for XO generation.

The significant disadvantage is that the alkali salt was found to be converted into irrecoverable salts that may be absorbed by the biomass during the pre-treatment process. The presence of a large amount of salt is a challenging issue for alkaline hydrolysis (Zheng *et al*., 2009). This method can be improved by the addition of other chemicals such as urea (Zhao *et al*., 2008) or in combination with other pre-treatment methods. Acid pre-treatment (removal of hemicellulose) followed by alkali pre-treatment (removal of lignin) results in a relatively pure cellulose.

Organosolv Pre-treatment

The organosolvation pre-treatment method has drawn a lot of attention since it has the potential for utilisation in lignocellulosic chemicals. In organosolv pre-treatment, organic solvents are used to extract lignocellulosic chemicals, where the solvent will increase the pore of the biomass and enhances accessibility to the surface area of lignocellulosic biomass and significantly reduce the lignin contents (Zhao *et al*., 2009). Organosolv pre-treatment usually operate at a range of 150°C-200°C. The most common solvent used in the pre-treatment process are ethanol, methanol, acetone, glycerol, aqueous phenol,ethylene glycol, triethylene glycol, aqueous n-butanol, tetrahydrofurfuryl alcohol, *etc*. (Taherzadeh and Karimi, 2008).

Ethanol is the most preferred solvent in industries due to its lower cost and low boiling point compared to other alcohols such as ethylene glycol, tetrahydrofurfuryl alcohol, *etc* (Arato *et al*., 2005). Ethanol also has low toxicity and easy to recover. Ethanosolv has been explored as an alternative to kraft pulping (Pye and Lora, 1991). Goh *et al*. (2011) have used aqueous ethanol [64% (w/w)] at 160°C-200°C for 45-90 min and obtained 96.3% recovery of glucose. Alroils *et al*. (2009) reported that they have used 80% of ethylene glycol in order to separate the cellulose, hemicellulose and lignin from OPEFB.

Through the organosolv process, the cost can be reduced by recycling the solvents from the process, but still there are potential hazards in handling such large volumes of organic solvents that limits the utilisation of pretreatment process.

PHYSICO-CHEMICAL PRE-TREATMENT

The physico-chemical processes are the improvements of existing chemical processes, to reduce reaction time and improve the efficiency of the process. In order to enhance the removal of lignin and increase their efficiency, physical parameters such as pressure and temperature are added to the established chemical pre-treatment. In previous studies, various types of physico-chemical pre-treatments for oil palm lignocellulosic biomass were used. These included pre-treatments such as ultrasonic, microwave, ball milling, superheated and chemical thermo-mechanical. A brief description of these technologies is given below.

Ultrasonic Pre-treatment

Ultrasonic pre-treatment is relatively new in lignocellulosic biomass pre-treatment technology. The effect of ultrasound on lignocellulosic biomass is to enhance the extractability of hemicelluloses, cellulose or lignin component. It is also used to clean cellulosic fibre from used paper and to improve the susceptibility of lignocellulosic materials to biodegradation by using ultrasound power (Asakura *et al*., 2008). Besides that, it can generate a pre-treated substrate to be more easily hydrolysed via increasing the accessible surface area and influencing the crystallinity (Toma *et al*., 2007). In order to determine the optimal conditions of ultrasonic exposure for the pre-treatment of lignocellulosic biomass, the efficiency of acid hydrolysis has been evaluated. Previous research done by Robiah *et al*. (2010) have found that a maximum xylose yield of 58% was achieved when the OPEFB fibre was ultrasonicated at 90% amplitude for 45 min. The hydrolysis occurred at a low temperature using 2% sulphuric acid; 1:25 solid-liquid ratio and 100°C operating temperature.

Microwave Pre-treatment

The combined microwave-chemical pre-treatment of different feedstock resulted to higher sugar recovery. Several chemicals were used in microwave/chemical pre-treatment such as microwave-assisted dilute ammonia (Chen *et al*., 2012) and microwave-assisted $FeCl_3$ (Lu and Zhou, 2011). Recently, there are two most commonly studied chemical methods in the pre-treatment of lignocellulosic biomass which are the microwave assisted-alkaline and microwave-assisted acid pre-treatments. In previous research done by Komolwanich *et al*. (2014), pre-treatment on OPEFB was done using the combination of microwave and NaOH. It is found that the enzymatic saccharification of OPEFB was significantly improved by the removal of more lignin and hemicellulose and enhancing the cellulose accessibility during the pre-treatment. Researchers indicate that microwave drying with proper selection of power input, weight of drying material and drying time could increase the drying rate. As a result, it could save up to 50% of energy and significantly decrease the volatile organic compound emissions when compared with the conventional drying methods (Guanben *et al*., 2005). In fact, microwaves can dry wood strands under lower temperatures and higher rates to produce dried wood with uniform and less moisture content and more permeability (Nomanbhay *et al*., 2013; Torgovnikov and Vinden, 2002; Vermaas, 1995). It should suffer from less shrinkage and swelling, as compared to that produced by kiln drying and traditional methods which are much more time consuming and less cost-effective (Guanben *et al*., 2005; Leiker and Adamska, 2004; Zhang *et al*., 1997). It can be concluded that although the microwave energy consumption is relatively higher than that of oven drying based on watt/hr^{-1}, it can be considered that much lower time will make the total energy consumed to be significantly lower than that of conventional methods (Ethaib *et al*., 2015). Research done by Parisa *et al*. (2010) showed the effectiveness of microwave drying in reducing the time and better removal of moisture as compared to that of oven drying. They were able to get the optimum conditions at 6.89 min with a microwave power for a 1000 g sample and with 14.62% of moisture content.

Ball Milling Pre-treatment

Ball milling is one of the most commonly used mechanical activation processes to increase the surface area of lignocellulosic biomass. Particle sizes and crystallinity index values of the OPB were significantly reduced with extended ball mill processing time. When OPF fibre was pre-treated through ball mill, it produced glucose and xylose yields of 87% and 81.6%, respectively, while OPEFB produced glucose and xylose yields of 70% and 82.3%, respectively (Zakaria *et al*., 2014a). This makes milling a good choice as a preliminary pre-treatment method for a wide variety of lignocellulosic feedstocks.

Superheated Steam Pre-treatment

Superheated steam (SHS) can be an alternative treatment method for lignocellulose. SHS treatment is advantageous compared to steam explosion as it is conducted at atmospheric pressure. Currently, SHS has been mainly used for drying (Schwartze and Brocker, 2002; Hasibuan and Wan Daud, 2009). Previous work on the use of SHS for treating OPB in order to ease the enzymatic hydrolysis of the lignocellulose for sugar production has been reported (Nik Mahmud *et al*., 2013; Bahrin *et al*., 2012). These studies were done to reveal the potential of SHS as a novel and alternative treatment method for modification of lignocellulose towards biocomposite production. The treated OPMF obtained in these studies was analysed for its chemical component, thermal stability, chemical structure and morphological characteristic. Bahrin *et al*. (2012) have claimed that their research on SHS treatment of OPEFB for fermentable sugars production is the first to be reported.

Overall, the results obtained suggested that SHS is an effective treatment method for surface modification and subsequently improving the characteristics of the natural fibre. Most importantly, the use of novel, eco-friendly SHS may contribute to the green and sustainable treatment for surface modification of natural fibre (Ahamad Nordin *et al*., 2013).

Chemical Thermal Mechanical Pre-treatment (CTMP)

There are various methods of treatments that can be used for the removal of silica bodies from the surface of OPEFB fibres; heat treatment, chemical treatment and mechanical treatment. Robiah *et al*. (2010) treated the OPEFB fibres by using a combination of heat and chemical treatment; acid hydrolysis at 100°C and ultrasonic pre-treatment. On the other hand, Rosman *et al*. (2013) treated the OPEFB using alkali followed by silane treatment and found that the surface treatment of OPEFB fibres increases the compactibility with the matrix, thus producing superior mechanical properties of the reinforced polymer composite. The modifications of OPEFB fibres treated with sodium hydroxide and succinic acid increased the availability of functional groups through chemical modification, and interacted strongly with the matrix polymer to get better interfacial bonding between fibres and matrix (Bhat *et al*., 2011). Zawawi *et al*. (2015) reported that the effects of pre-treatments on the surfaces of EFB fibres are subjected to thermomechanical pulping (TMP) process. For fibres treated with NaOH, the SEM images showed that alkali treatment made the fibre surface rougher with less amount of silica bodies. Most of the lignin and small amount of silica bodies were removed resulting in a rough surface. A study done by Ariffin *et al*. (2008) claimed that the combination of physical, chemical and thermal pre-treatments have successfully altered the physical structure and chemical composition of the OPEFB, as well as in reducing sugar production. OPEFB treated by chemical treatment followed by thermal is the best treatment in order to produce the reducing sugars as compared to the reversed pre-treatment technique.

BIOLOGICAL PRE-TREATMENTS

In comparison with the conventional chemical and physico-chemical pre-treatment methods, biological pre-treatment is considered as an efficient, environmentally safe method as it has no requirement for chemicals and needs only mild environmental conditions employed as well as low-energy process. Substrate specificity and simple process and equipment requirements are other advantages that have been reported (Kirk and Chang, 1981). Biological pre-treatments are carried out by microorganisms such as brown-rot fungi, white and soft-rot fungi as well as bacteria, and their enzymes system, which mainly degrade lignin and hemicellulose and a little amount of cellulose (Vats *et al*., 2013; Ray *et al*., 2010; Hamisan *et al*. 2009; Kurakake *et al*., 2007; Taniguchi *et al*., 2005; Hataka, 1983). Recently, this environmental-friendly approach has received renewed attention as a pre-treatment technique for enhancing enzymatic hydrolysis for various lignocellulosic biomass. However, literature review has indicated that limited studies have been conducted on biological treatment of OPB.

Microorganisms Pre-treatment

The most intensively investigated microorganisms in the biological pre-treatment of lignocellulosic biomass are the white fungi as their ligninolytic enzyme could degrade lignin efficiently (Isroi *et al*., 2011; Tanaguchi *et al*., 2005; Zadražil and Puniya, 1995; Martinez *et al*., 1994). Microbial pre-treatment using Phanerochaete chrysosporium ATTCC 32629, showed significant lignin removal from OPEFB with an optimum value of 5.89 Klason lignin. Nevertheless, for the same value of Klason lignin, delignification by chemical pre-treatment needs only 3 hr as compared to seven days for microbial pre-treatment. It is also reported that the lignin removal is dependent on the microbial ability, either to consume lignin or to produce biological products such as enzymes, to remove lignin (Hamisan *et al*., 2009). Isroi *et al*. (2012) studied a single biological pre-treatment and a combination of phosphoric acid and biological treatment on OPEFB. Biological pre-treatment was carried out using the white-rot fungus *Pleurotus floridanus*. The composition of OPEFB was slightly changed by the fungal pre-treatment, but it was significantly altered by the fungal followed by phosphoric acid pre-treatment. The fungal pre-treatment resulted in the least losses of both total solid (1.31%) and total carbohydrates (7.89%) compared to the combined pre-treatment of fungal followed by phosphoric acid; the losses of total solid and total carbohydrates were correspondingly 63.55% and 33.77%. Thus, using fungal pre-treatment, much more lignocellulosic material remains to be utilised, and it has less environmental impacts.

Enzymatic Pre-treatment

Generally, enzymatic pre-treatment is given to the lignocellulosic biomass prior to the subsequent process for lignin degradation, hence cellulose will become more accessible. Amin *et al*. (2010) studied the effect of enzymatic pre-treatment on OPEFB prior to the pyrolysis process for degrading the lignin structures. The percentage lignin degraded by lignin peroxidase (LiP) enzyme and manganese peroxidase (MnP) enzyme were recorded at 71.69% and 67.94%, respectively. The enzymatic treated OPEFB have resulted in higher bio-oil yield (30 wt%) compared to the untreated sample (20 wt%). Nazlee *et al*. (2017) reported that it is possible to produce sugars from the cellulose of OPEFB fibre by enzymatic hydrolysis in membrane reactor. The cellulolytic complex enzyme commercially known as Celluclast 1.5L (Novozymes) when employed was able to increase productivity from 0.003 to 0.01 g reducing sugars/FPU enzyme in batch reactor and enzymatic reactor. The reusability of cellulose enzyme was also reported up to 216 hr in enzymatic membrane reactor.

GREEN PRE-TREATMENT

A technology that reduces or eliminates the hazardous chemicals used as well as an application of safer solvent and safer reaction conditions would qualify it as a green treatment. The use of green technology to recover lignocellulosic chemicals from the OPB is to reduce environmental impact. The extraction of lignocellulosic chemicals using processes that employ less solvent at low concentration, less toxic and non-toxic feedstock selections in combination with physical treatments that are less energy intensive, are considered as green methods. In addition, ionic liquid, ozonolysis and hydrothermal pre-treatments also can be categorised as green methods as these methods eliminate the chemical usage.

Eco-friendly Reagents

Organic acids such as acetic acid and formic acid are eco-friendly reagents, less corrosive and effective for the pre-treatment of lignocellulosic biomass, and they provide a more stable medium for monosaccharide in the aqueous phase as compared to sulphuric acid (Marzialetti *et al*., 2011). The application of low concentrations of 20% (v/v) formic acid and 10% (v/v) of 30% hydrogen peroxide at 85°C for the extraction of cellulose from OPEFB produced a total cellulose yield of 64% (w/w), which was among the highest ever reported (Nazir *et al*., 2013). The extraction of cellulose fibres from OPEFB by hydrogen peroxide with an ultrasound-assisted alkali extraction yields 49% of cellulose (Nazir *et al*., 2012). The utilisation of eco-friendly reagents as an alternative to acidified sodium chlorite for the delignification and the extraction of cellulose from OPEFB will reduce the environmental impacts of hazardous chemicals. Besides that, low concentration of chemicals is being used resulting in low operating cost and this also is one of the advantages associated with this treatment.

Ionic Liquids

Ionic liquids are new organic salts, which generally exist in a liquid state at ambient temperature due to their low melting points. Principally, useful characteristics such as high ionic conductivity, high solvation power, thermal stability, inflammability, low volatility confer the status 'green solvent' on ionic acid for various chemical reactions in industrial processes (Rabemanolontsoa and Saka, 2016; Zhu *et al*., 2006; Heinze *et al*., 2005).

The development of a novel process that uses ionic liquid {1-butyl-3methylimidazolium chloride [(Bmim)Cl]} followed by alkaline treatment to extract cellulose from OPEFB fibre with 93% α-cellulose recovery has been reported (Norzita and Lani, 2014). The improvement in the properties of cellulose obtained was observed to be 63% crystallinity with thermal decomposition step occurred at 390°C. Thus, this process represents an efficient treatment in extracting cellulose with better properties and having the highest yield. In another study, the same types of ionic liquid; (Bmim)Cl employed in the liquefaction process with sulphuric acid as a catalyst, managed to extract 26.6% lignin from EFB. The utilisation of recycled ionic liquid in the process showed no significant reduction of lignin yield (Sidek *et al*., 2013). Tan *et al*. (2011) studied the optimisation of glucose recovery from OPF by subjecting the OPF into ionic liquid (Bmim)Cl prior to cellulose regeneration by an anti-solvent. An optimum 100% glucose recovery was obtained with pre-treatment conditions of 80°C, a 15 min retention time and 10% solid loading by employing a response surface methodology. Mohd Basyaruddin *et al*. (2012) investigated the application of two different ionic liquids; namely 1-butyl-3-methylimidazolium chloride/dimethyl sulphoxide and 1-ethyl-3-methylimidazolium chloride/dimethyl sulphoxide on the swelling and dissolution of OPB and cellulose fibre from OPEFB, OPF and OPT. These OPB fibres treated with ionic liquids showed homogeneous swelling without dissolution, whereas the cellulose fibre from these OPB has been attributed to the subsequent swelling and dissolution mechanisms of the fibre when subjected to the ionic liquids. Lignin extraction from OPB, namely OPEFB, OPT and OPF by dissolution in ionic liquid; 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) followed by precipitation in various precipitating agent was reported by Mohtar *et al*. (2015). The lignin from these OPB was successfully extracted by ionic liquid dissolution and non-toxic CO_2 – aluminum potassium sulphate dodecahydrate [$(AlK(SO_4)_2.12H_2O$] precipitation process with the highest lignin yield was observed for OPT.

Ionic liquids can be claimed to be potential solvents in dissolving cellulosic materials, and have high potential as one of the green routes towards volatile organic solvent replacement. Regardless of their promising chemical properties, ionic liquids present the drawback of being expensive and require tedious recycling and reuse, since their toxicity and biodegradability are not well understood (Kumar and Sharma, 2017; Rabemanolontsoa and Saka, 2016).

Ozonolysis

Ozonolysis is an ozone treatment which is mainly used for reducing the lignin content of lignocellulosic biomass as it mainly degrades lignin, but negligibly affects hemicellulose and cellulose. The use of ozone treatment can be classified as a greener technology as this process produces no toxic residues and it is performed at ambient temperature and pressure (Kumar *et al*., 2009). Also, it does not produce any toxic inhibitors, therefore it is environment-friendly and does not affect the post-treatment process such as enzymatic hydrolysis and yeast fermentations (Quesada *et al*., 1999). This technique degrades most of the lignin and some of the hemicellulose, while leaving the cellulose intact. Some researchers conducted their research in this eco-friendly method with wheat straw (Ben and Miron, 1981), bagasse, green hay, peanut, pine (Neely, 1984) and poplar sawdust (Vidal and Molinier, 1988). However, a large amount of ozone utilisation in the treatment makes it an expensive process, and hence a less suitable option for pre-treatment at industrial scale (Kumar *et al*., 2009). Not much work on ozonolysis treatment of OPB is reported in the literature. Wan Omar and Amin (2016) studied the optimisation of lignin degradation and total reducing sugar recovery from OPF by ozonolysis pre-treatment by manipulating several operating conditions such as OPF particle size, moisture content, reaction time, ozone flow rate as well as their interaction by employing a response surface methodology. The optimum lignin degradation and total reducing sugar recovery were achieved at 84.7% and 99.9%, respectively; with the levulinic acid production from the pre-treated OPF was comparable to that of commercial cellulose.

Hydrothermal Pre-treatment

A new emerging green technology known as hydrothermal treatments, commonly defined as reactions occurring under the conditions of high temperature and high pressure in aqueous solutions in a closed system (Rabemanolontsoa and Saka, 2016). The hydrothermal pre-treatment is widely applied on various lignocellulosic biomass to enhance their enzymatic digestibility as most of the hemicelluloses and partial lignin can be removed before the cellulose degrades under hydrothermal condition (Sun *et al*., 2016). The process temperatures are usually ranging from 160ºC to 240ºC as the cellulose degradation normally occurs at a temperature higher than 240°C (Cao *et al*., 2014; Sun *et al*., 2014). The system only uses water and the hydronium ion from water ionisation acts as a catalyst in the reaction medium (Möller *et al*., 2011; Sabiha-Hanim *et al*., 2011). Due to that reason, this method, is recognised as one of the most promising and environmental-friendly biomass pre-treatment methods available to make the lignocellulosic biomass susceptible to a subsequent process for fermentable sugars production. The hydrothermal pre-treatment is categorised into the steam explosion, liquid hot water or also referred to as hot compressed water as well as supercritical/subcritical water depending on the conditions of temperature and pressure involved (Kumar and Sharma, 2017; Rabemanolontsoa and Saka, 2016).

Zakaria *et al*. (2015a) studied the effect of varying temperature (170°C to 250°C) and time (10 to 20 min) during hydrothermal pre-treatment in a batch tube reactor system on the glucose production from OPEFB and OPF fibre. Partial removal of hemicellulose and migration of lignin of treated samples resulting to expansion of the surface area and creation of pores for easy access to enzymes during enzymatic hydrolysis, thus enhancing the yield of glucose at 87.9% conversion from OPF fibre and 100% conversion from OPEFB. In another study also carried out by Zakaria *et al*. (2014b), they reported that a combined pre-treatment using hydrothermal and ball milling on OPMF in the tube reactor could improve hemicellulose removal and delignification as well as reduction in the cellulose particle size and its crystallinity. The highest yield of xylose and glucose obtained in the enzymatic hydrolysis on the treated sample were recorded at 63.2% and 97.3%, respectively, which is the highest conversion from OPMF ever reported. Two different hydrothermal pre-treatments, namely SHS and HCW with a combination of wet disk milling (WDM) on OPMF were developed by Zakaria *et al*. (2015b). It was reported that the combination of HCW and WDM offered shorter milling cycles and lower power consumption with more than 98% of glucose yield. This eco-friendly combined pre-treatment is using hydrothermal and WDM to enhance the enzymatic efficiency of OPMF and claimed as the first to be reported. In an effort to overcome the difficulty of OPEFB degradation in a short period-time, hydrothermal pre-treatment has been developed under different reaction temperature (100ºC -250ºC), reaction time (10-40 min), solid to solvent ratio (1:10 - 1:20 w/v) and particle size (0.15-1.00 mm). The highest yield of soluble sugars at 68.18 mg glucose per gram of OPEFB was obtained at 178ºC, 20 min reaction time, 1:15 w/v of solid to solvent ration for 30 mm of particle size (Muhd Ali *et al*., 2016). A pre-treatment of OPF using HCW to enhance glucose recovery in enzymatic hydrolysis as a feedstock for bioethanol production has been studied by Goh *et al*. (2010). An application of central composite rotatable design for the process optimisation found that the optimum yield of glucose (92.78%) was recorded at temperature of 178°C, 11.1 min reaction time and a liquid-solid ratio of 9.6 in a 10 bar pressurised reactor. Limited or no chemicals usage and environment-friendly process are the main advantages of the hydrothermal pre-treatment method. Despite their green process, hydrothermal presents the drawback of being costly, since it consumes high energy and water. The formation of toxic compounds to microorganisms and enzymes which impact the subsequent fermentation process is also a disadvantage associated with the hydrothermal pre-treatment (Sun *et al*., 2014; Brodeur *et al*., 2011).

Summary of Lignocellulosic Oil Palm Biomass Pretreatments

The main goal of numerous pre-treatment strategies that have been developed for OPB is to enhance the reactivity of cellulose and to increase the yield of fermentable sugars. The advantages and disadvantages of different pre-treatment methods are listed in *Table 2*.

TABLE 2. ADVANTAGES AND DISADVANTAGES OF DIFFERENT PRE-TREATMENT METHODS ON OIL PALM BIOMASS (OPB) LIGNOCELLULOSE

Pre-treatment method	Advantages	Disadvantages
Chemical		
Acid	(i) High glucose yield (ii) Solubilises hemicellulose	(i) High costs of acids and need for recovery (ii) High costs of corrosive resistant equipment (iii) Formation of inhibitors
Alkali	(i) Efficient removal of lignin (ii) Low inhibitor formation	(i) High cost of alkaline catalyst (ii) Alteration of lignin structure
Organosolv	(i) Lignin and hemicellulose hydrolysis (ii) Ability to dissolve high loadings of different biomass types (iii) Mild processing conditions (low temperatures)	(i) High solvent costs (ii) Need for solvent recovery and recycle
Physico-chemical		
Ultrasonic	(i) Green and sustainable treatment	(i) Incomplete disruption of the lignin-carbohydrate matrix
Microwave	(i) Less inhibitor formation (ii) High reaction rate and yields	(i) High energy/cost
Ball milling	(i) Green and sustainable treatment	(i) Incomplete disruption of the lignin-carbohydrate matrix
Superheated steam	(i) Cost-effective (ii) Lignin transformation and hemicellulose solubilisation (iii) High yield of glucose and hemicellulose in two-step process	(i) Partial hemicellulose degradation (ii) Acid catalyst needed to make process efficient with high lignin content material (iii) Toxic compound generation
Chemical thermal mechanical pre-treatment (CTMP)	(i) Green and sustainable treatment	(i) Involve more than two steps for pre-treatment (ii) Require more reaction time
Biological		
Microorganism	(i) Environmentally save (ii) No chemicals needed (iii) Efficient removal of lignin, hence cellulose becomes more accessible (iv) Gentle process (v) Low energy requirement (vi) Substrate specificity (vii) Simple process and equipment requirements	(i) Low in degradation rate (ii) Longer pre-treatment time

TABLE 2. ADVANTAGES AND DISADVANTAGES OF DIFFERENT PRE-TREATMENT METHODS ON OIL PALM BIOMASS (OPB) LIGNOCELLULOSE (continued)

Pre-treatment method	Advantages	Disadvantages
Enzyme	(i) Mild processing conditions (low temperature) (ii) Low energy requirement (iii) Environmental-friendly (iv) Efficient in lignin degradation (v) Specifically substrate targeted/higher selectivity	(i) Longer treatment time (ii) Low in hydrolysis rate (iii) Expensive process due to the high cost of enzyme used
Green		
Ionic liquid	(i) Green solvent – no harmful to environment (ii) Less amount of solvent needed (iii) Recyclable (iv) Low viscosity, non-volatility, non-flammability (v) Shorter processing time	(i) High cost of solvent
Ozonolysis	(i) Eliminates the use of hazardous chemicals (ii) Efficient in lignin removal (iii) No formation of toxic residues and toxic inhibitors (iv) Operation at ambient temperature and pressure (v) Cellulose becomes more accessible	(i) Require large amount of ozone (ii) Expensive process
Hydrothermal	(i) Cost-effective process (ii) Environmentally benign (iii) Non-toxic, non-flammable, non-carcinogenic, non-mutagenic and thermodynamically stable (iv) Increase cellulose accessible area	(i) Partial hemicellulose degradation (ii) Production of inhibitory compounds to microorganisms and enzyme (iii) High water input

CONCLUSION

Lignocellulose has a highly crystalline and recalcitrant structure, as well as the presence of lignin in the OPB make the hydrolysis of cellulose and hemicellulose extremely difficult. Hence, various pre-treatment techniques for delignification of OPB have been developed. Common observed outcomes of pre-treatments include the decrease of lignin content, increase of surface area and the decrease of crystallinity of the biomass; all of which result in enhancing all of the subsequent processes (enzymatic saccharification and fermentation). This review focuses on chemical, physical, biological and their combination pre-treatment processes along with their advantages and disadvantages, and it will help the researchers in planning, selecting and developing the pre-treatment process for successful OPB conversion. This review also emphasises on the use of OPB as renewable and sustainable source of material for the production of value-added products, such as lignocellulosic chemicals, thus generating additional revenue for the country. This would diversify the utilisation of OPB, which is normally used for biofertiliser and solid biofuel.

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